Alberta

Technologies to Recover and Use Alberta's Sulphur Resources

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Cover Photo: Sulphur, once regarded as a nuisance by-product of sour gas processing, has become a valuable commodity in Alberta. Some recent sour gas projects were initiated principally because of the high sulphur content of the natural gas.

Technologies to Recover and Use Alberta's Sulphur Resources

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Foreword

Since 1976, numerous projects have been initiated in Alberta by industry and by academic research institutions which are aimed at better utilization of Alberta's energy resources.

These research, development and demonstration efforts were funded by the Alberta/Canada Energy Resources Research Fund (A/CERRF), which was established as a result of the 1974 agreement on oil prices between the federal government and the producing provinces.

Responsibility for applying and administering the fund rests with the A/CERRF Committee, made up of senior Alberta and federal government officials.

A/CERRF program priorities have focused on coal, energy conservation and renewable energy and conventional energy resources. Administration for the program is provided by staff within the Scientific and Engineering Services and Research Division of Alberta Energy.

In order to make research results available to industry and others who can use the information, highlights of studies are reported in a series of technology transfer booklets. For more information about other publications in the series, please refer to page 13.

Technologies to Recover and Use Alberta's Sulphur Resources

Elemental sulphur, produced as a by-product of sour gas processing, has become a valuable resource for Alberta. It is used primarily as a raw material in the chemical and fertilizer industries, and its principal source is natural gas that contains hydrogen sulphide, an unpleasant smelling chemical which gives "sour gas" its name.

Because sulphur production is dependent on sour gas processing, and sulphur markets tend to fluctuate with demand for agricultural and chemical products, sulphur reserves and prices tend to rise and fall with changes in commodity markets. To help offset these trends, more efficient sulphur recovery processes and new markets for sulphur are being sought.

To some extent, these efforts have been supported by the Alberta/Canada Energy Resources Research Fund.

Development of the Pronk Sulphur Asphalt Paving Process

New markets for sulphur have resulted from the efforts of the Sulphur Development Institute of Canada (SUDIC), a non-profit research and market development corporation funded by industry and government and based in Calgary. One of the Institute's successful developments is a sulphur-extended asphalt paving material invented by F.E. Pronk of Calgary and subsequently named the Pronk Sulphur Asphalt Paving Process.

Background

In 1973, when work began on the Pronk Process, it was one of several sulphur asphalt paving systems undergoing development. In the other formulations, sulphur acted as an additive to allow replacement of high quality paving aggregates with low quality materials, such as sand, without sacrificing strength of the resulting pavement.

The economics of these processes depended upon the relative costs of high quality aggregates versus sand/sulphur mixtures. For example, a typical formulation used six per cent asphalt, 13 per cent sulphur and 81 per cent sand, whereas standard asphalt mixes were comprised of six per cent asphalt and 94 per cent aggregate.

The handling characteristics of such sulphur-based mixes tended to be different from normal asphalt mixes, sufficiently so that some modifications to the paving process were necessary.

In the Pronk Process, molten sulphur is dispersed in liquid asphalt to form an emulsion which acts as a binder, thereby allowing displacement of up to 31 per cent of the normal asphalt content, which can result in cost savings directly proportional to the relative costs of asphalt and sulphur. A typical Pronk formulation consists of seven per cent binder (comprised of 40 per cent sulphur and 60 per cent asphalt) and 93 per cent aggregate.

Because surface-active agents (organosiloxane polymers) are used to promote sulphur dispersion and enhance the formation and stability of the binder emulsion, Pronk mixes can be handled in the same manner as standard asphalt mixes. Also, the low viscosity of Pronk binders allows aggregates to be coated at the asphalt plant and then compacted at the paving site at lower temperatures than usual, thereby saving up to 15 per cent of normal heating fuel requirements.

Pronk sulphur asphalt pavement has been found to be stronger than conventional asphalt pavement, although it is somewhat stiffer. Over good subgrades where pavement deflections are likely to be low, the thickness of Pronk pavement can be reduced. Tests showed that each ton of Pronk mix can replace up to 1.25 tons of regular asphalt. Alternatively, the load-bearing characteristics of mixes made with marginal aggregates can be improved by using the Pronk Process.

Characteristics which suggested the Pronk Process may have worldwide application due to cost reduction and energy savings prompted the A/CERRF Committee to assist SUDIC in demonstrating the concept on a commercial scale.

Study Objectives and Results

The primary objective of the A/CERRF-funded portion of this development program was to undertake a major field placement of Pronk sulphur asphalt mix. This would establish the suitability of the process for continuous production using conventional, commercial-scale equipment and allow long-term evaluation of the material's performance under typical traffic conditions. The study also addressed other aspects of the process, such as procedures for determining the sulphur-to-asphalt ratio and total binder content of mixes. As well, the fatigue properties of Pronk mixes were measured and compared with standard mixes, and measurements were made of gaseous sulphur compounds emanating from the stored binder and hot mixes.

Field Placement

In co-operation with Alberta Transportation, a section of a secondary road near Rocky Mountain House was paved with Pronk sulphur asphalt mix in late 1977, using conventional asphalt mix as control. Also, an additive-type sulphur asphalt formulation, developed by Gulf, was included in the placement test.

The Pronk sulphur asphalt mix was placed and compacted without difficulty. It was found that mixing could be performed at 125°C, which is 25°C below the normal operating temperature for batch plants. It was possible to prepare the emulsified binder separately and store it for a period of time, using only mild agitation to maintain the integrity of the emulsion.

A typical paving operation using Pronk Sulphur Asphalt

Emissions

Although eye-irritating emissions have been associated with some sulphur asphalt formulations, it was found that they are apparently suppressed in the Pronk Process. Furthermore, concentrations of sulphur dioxide and hydrogen sulphide at the mix plant and the paving site were well within exposure limits established by the Workers' Compensation Board.

Process Control

In modern drum mix plants capable of producing asphaltic concrete at more than 600 tons per hour, it is important to be able to quickly monitor and control the ratio of sulphur to asphalt and the binder content.

Under these circumstances, the conventional solvent extraction technique is inappropriate because of the time required to dissolve sulphur in trichloroethylene, the solvent used in the procedure. Alternatively, it might be possible to use a calibration curve relating specific gravity to the ratio of sulphur to asphalt but it, too, requires several hours to complete.

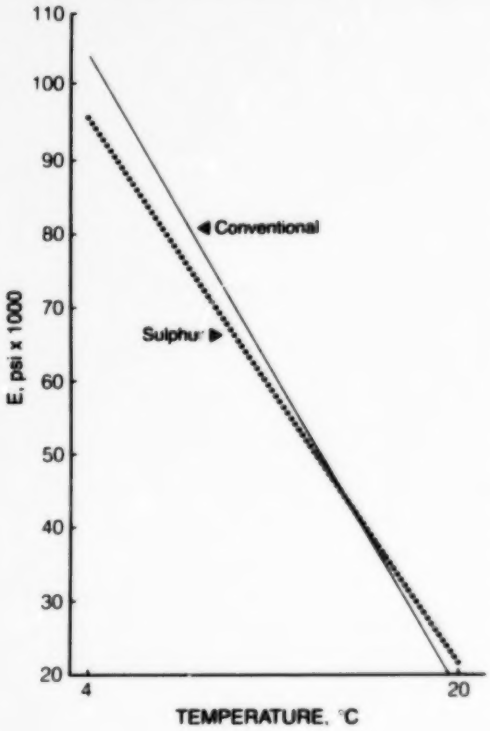
To obtain results in less time, a nuclear asphalt gauge was used during the field trials at Rocky Mountain House. In this analytical method, hydrogen atoms present in the asphalt slow down fast-moving neutrons emitted by a radioactive source. In this manner, the intensity of these moderated neutrons, as measured by a detector, is directly proportional to the hydrogen content, and thereby the asphalt content, of the mix.

The field trials showed satisfactory correlation between the results obtained from the nuclear asphalt gauge and from solvent extraction, leading the investigators to conclude that the nuclear asphalt gauge method is a rapid and reliable method of determining sulphur-to-asphalt ratios and total binder content.

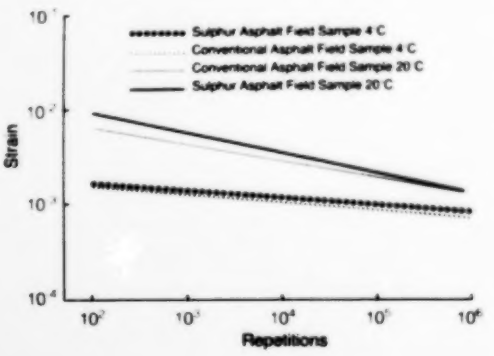
Fatigue Testing

Samples of Pronk sulphur asphalt pavement and conventional pavement were subjected to fatigue testing at the University of Saskatchewan. Some of the samples were prepared in SUDIC's laboratory, while others were removed from the field installation near Rocky Mountain House. Stress-mode fatigue testing was performed at 20°C and 40°C. After regression analysis of the data, it was concluded that the fatigue properties of Pronk sulphur asphalt mix appear to be equal to, if not superior to, conventional mixes. Also, the modulus of elasticity of Pronk mix samples is less temperature-sensitive than conventional mixes.

Elastic Modulus of Conventional and Sulphur Asphalt Field Samples



Fatigue Testing Results: Strain vs Repetitions


Sulphur Asphalt Field Sample 4 C
Conventional Asphalt Field Sample 4 C
Conventional Asphalt Field Sample 20 C
Sulphur Asphalt Field Sample 20 C
Strain
Repetitions

(Source: *Pronk Sulphur Asphalt Paving Mix*. Sulphur Development Institute of Canada. June 18, 1979)

Subsequent Developments

During the first year following placement of the test section of highway, cracks developed in several portions of the pavement due to subgrade failure and frost heaves, making it impossible to properly compare the performance of Pronk sulphur asphalt with conventional asphalt.

Subsequently, however, several large-scale trials were carried out at other locations in Canada and in the U.S. where quantities of Pronk sulphur asphalt ranging from 11 000 tonnes to 125 000 tonnes were used per project. Results of these trials were so encouraging that by the end of 1984, 87 per cent of all the sulphur-extended asphalt placed on North American highways (totalling 1.4 million tonnes) was the Pronk type. Consequently, several state and provincial governments approved the Pronk Process for highway use.

Meanwhile, SUDIC has been granted patent rights to the Pronk Process in approximately 12 countries, and SUDIC has developed other sulphur-containing products such as sulphur concrete and press-molded sulphur construction blocks. According to SUDIC, these projects, and others (including management studies), generated $1.2 billion worth of business for the sulphur industry between 1973 and 1983.

Since 1984, sour gas production in Alberta has been cut back somewhat, resulting in smaller inventories of sulphur. Also, sulphur prices have risen, making sulphur significantly less cost-competitive when compared with asphalt. As a result, few highways departments have opted for sulphur-extended asphalt pavement in recent years. This situation may remain static for some time because the Energy Resources Conservation Board forecasts little change in Alberta's sulphur inventory unless sulphur recovery from sour gas can be improved by using new technology, or alternative sources of sulphur are found.

Location of Commercial-Scale Applications of Sulphur Extended Asphalt Pavement (to December 31, 1984)

(Source: *Historical Review of Sulphur Extended Asphalt Pavement Construction in North America*, Sulphur Development Institute of Canada, December 31, 1984)

Evaluation of Claus Catalysts

The hydrogen sulphide (H_2S) found in sour gas is toxic in certain concentrations. For example, it is hazardous at concentrations above 150 parts per million, but, even at 20 parts per million it is an eye irritant. Therefore, it must be removed in a gas-processing plant before natural gas can be marketed. To remove it, the sour gas industry uses the Modified Claus Process which converts H_2S to elemental sulphur in the presence of heat and a catalyst.

The conversion occurs in two stages. In the first stage, hydrogen sulphide reacts with oxygen to form sulphur dioxide and water.

$$(1)\ H_2S + \frac{3}{2} O_2 \rightleftharpoons SO_2 + H_2O$$

In the second stage, hydrogen sulphide and sulphur dioxide react with each other to form sulphur and water.

$$(2)\ 2H_2S + SO_2 \rightleftharpoons \frac{3}{n} S_n + 2H_2O$$

where $S_n = S_2, S_3, \ldots S_8$

Also produced in the reaction are carbon disulphide (CS_2) and carbonyl sulphide (COS), both of which must be removed in subsequent cleanup stages or be incinerated to produce sulphur dioxide.

If the need for cleanup or incineration could be reduced or eliminated, it might be possible to reduce production costs, save energy and recover more sulphur. One way to accomplish this might be to convert CS_2 and COS to sulphur at an earlier stage in the process by using a catalyst which is compatible with the Modified Claus Process and also promotes conversion of CS_2 and COS.

In attempting to prepare such a "bifunctional" catalyst, researchers at the University of Alberta Department of Chemical Engineering found that addition of a specific metal to alumina (presently used as catalyst in the Modified Claus Process) produced a "novel" catalyst which, when compared with alumina itself, improved H_2S/SO_2 conversion by up to 50 per cent but resulted in less COS conversion. These laboratory results were thought to be promising, especially because plant conditions should favor greater conversion of COS. To encourage further development, A/CERRF and the Canadian Gas Processors Research Fund provided financial assistance to carry out a pilot plant comparison of the performance of alumina and the novel catalyst.

The two catalysts were tested at the Nevis gas plant (operated by Gulf Canada Resources Inc.) in a pilot facility consisting of twin reactors operated in parallel with the plant's first-stage converter.

Although there was considerable variation in the subsequent results, caused by changing conditions at the plant, which made direct comparisons difficult, the researchers concluded the novel catalyst is superior to alumina. This is because the novel catalyst is more reactive, causing comparable or better conversion of H_2S and SO_2 at lower temperatures with significantly less reaction time, thus allowing more gas to be handled in a specified period of time. Unlike laboratory conditions, it was found the novel catalyst was comparable to alumina in converting COS and CS_2.

After the results of this investigation were made public in 1983, commercial production of the novel catalyst was pursued by industry.

A typical Modified Claus plant at a sour gas processing facility.

Production of Hydrogen and Sulphur from Hydrogen Sulphide

When the hydrogen sulphide (H_2S) in sour gas is converted by the Modified Claus Process, one of its elements, sulphur, is recovered but the other hydrogen, is lost because it is converted into water. However, if sour gas could be treated in some manner to allow recovery of sulphur and hydrogen, another valuable commodity could become available in large quantities for use as an energy source or for petrochemical processing such as the hydrodesulphurization of high-sulphur fossil fuels.

To determine the feasibility of simultaneously recovering both of these substances, researchers at the University of Calgary, Department of Chemistry, investigated a method of decomposing H_2S using high temperatures and catalysts.

In the laboratory, they used thermal diffusion columns which allowed sulphur to condense on a cool surface within the column, and also permitted hydrogen to become separated from unreacted H_2S by means of thermal diffusion toward one end of the device.

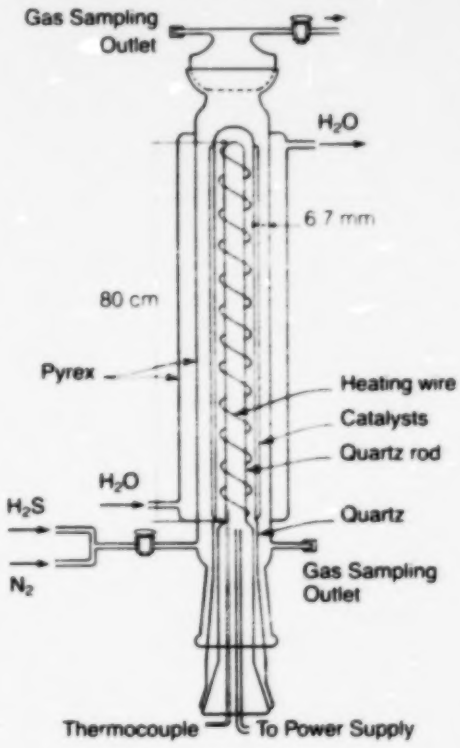
A variety of reaction conditions was tried, as well as several column configurations until a set of conditions was reached that gave hydrogen yields of 78 to 91 per cent, in the temperature range of 700 to 800°C, in the presence of a catalyst comprising molybdenum sulphide and alumina.

Based on these promising results, the commercial potential of this thermal diffusion concept was assessed but it was found that high heat losses incurred in the thermal diffusion column would be unacceptable on a commercial scale.

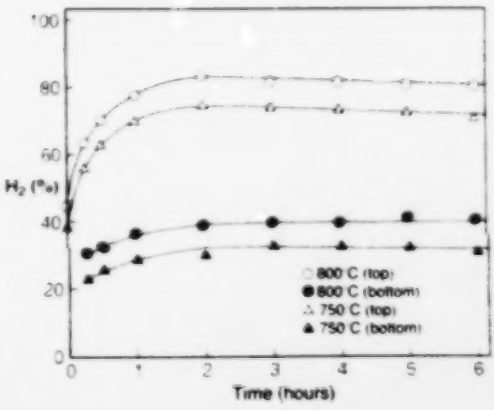
This prompted the researchers to raise the temperature of the sulphur collector inside the thermal diffusion column to reduce heat loss. It also allowed sulphur to be recovered in a liquid state, thus facilitating its removal. Also, the thermal diffusion concept was incorporated in a gas fluidized-bed reactor design that allowed rapid heat transfer.

Unfortunately, neither of these modifications was able to overcome the loss of large amounts of heat. However, the investigators are optimistic that a better understanding of the decomposition mechanism may lead to operating conditions which are less severe and incur tolerable heat losses.

Thermal Diffusion Column



Hydrogen Yields Versus Time for MoS_2 + Alumina Using Thermal Diffusion Column



(Source: *Production of Hydrogen and Sulphur From Hydrogen Sulphide*, Chivers, T. and C. Lau, March 31, 1980)

Sulphur Plant Studies

Since 1968, extensive research projects on all aspects of the Modified Claus Process have been carried out by Western Research and Development and Bow Valley Research Ltd., both of which are divisions of Calgary-based Bow Valley Resource Services Ltd. Several of these studies were funded by A/CERRF.

Capability of the Modified Claus Process

In March 1979, Western Research and Development published a 180-page summary of sulphur plant investigations which took place over a 12-year period. Entitled "Capability of the Modified Claus Process," the document contains an analysis of current technology, made possible by the development of a realistic thermodynamic model of the Modified Claus Process and effective test procedures to evaluate performance of the process. Using a body of knowledge based on 250 sulphur plant performance tests, 760 source emission tests for sulphur dioxide, and fuel consumption studies on 18 sulphur plant incinerators, the publication is a valuable guidebook for process operators and designers. It was used as the primary reference text for sulphur plant seminars that have been held during intervening years in Alberta, several U.S. states, Amsterdam and Singapore.

In the process of solving problems related to sampling, analysis and data reduction, Western Research and Development designed and marketed a patented, continuous stack emission monitor, a computer-controlled sulphur plant process optimizer, a family of photometric gas analyzers and an automated control system for sulphur plants.

Tail Gas Incineration

After sour gas has been subjected to the Modified Claus Process, the remaining "tail gas" is incinerated. This produces sulphur dioxide, which is expelled to the atmosphere in concentrations which must satisfy limits established by environmental protection authorities. Because "tail gas" contains small and variable amounts of combustibles, it is mixed with natural gas in amounts sufficient to support combustion and to achieve temperatures capable of completely oxidizing all the components of the gas mixture. This results in the consumption of large quantities of natural gas, some of which might be conserved by altering the incineration process. For instance, in 1977 (when this study began) tail gas incineration at Alberta's sulphur plants consumed enough natural gas to satisfy the needs of half the homes in Calgary.

An investigation of incineration kinetics showed it was possible to reduce natural gas consumption by 40 per cent by optimizing the operation of typical sulphur plant incinerators. However, it was not possible to establish one set of optimum conditions that would apply to the wide diversity of incinerator designs, sizes and operating circumstances which characterize Alberta's sour gas industry. Nevertheless, incinerator operation at 13 sulphur plants was altered as a result of this study, causing a reduction in fuel consumption which averaged 39 per cent.

Alternative Incineration Processes

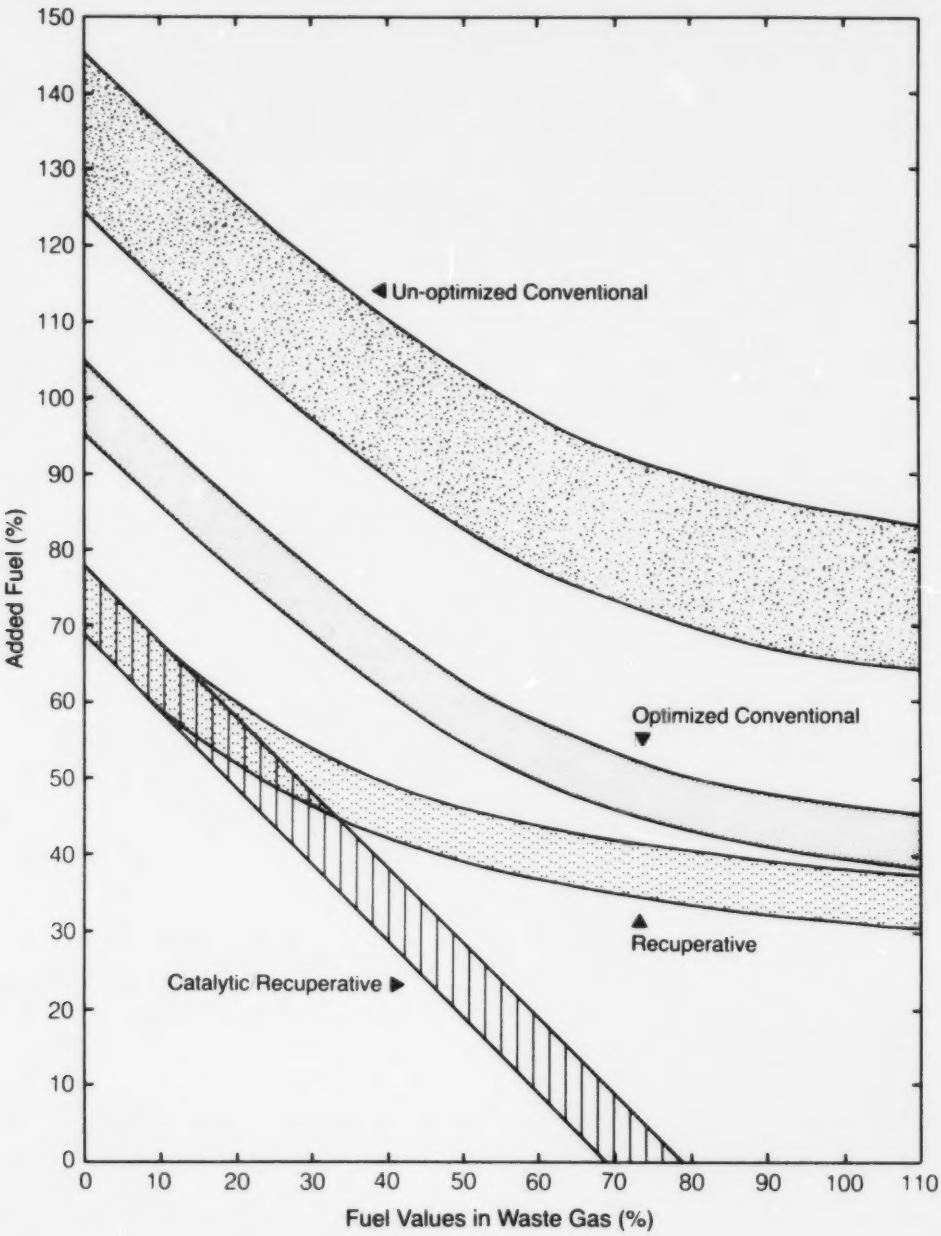
Recuperative Heat Exchange

Laboratory studies showed natural gas usage could be reduced even further — by an additional 50 to 70 per cent — by incorporating recuperative heat exchange into the tail gas incinerator. This allows some heat to be transferred from the exhaust gas to the tail gas as it enters the incinerator, thereby reducing the quantity of fuel and primary air required to maintain the desired combustion chamber temperature.

Catalytic Incineration

Other laboratory-scale investigations revealed that additional fuel savings were possible if catalytic incineration were employed when tail gas contains greater amounts of combustibles. This allows elimination of the continuous-burning flame normally used to provide mixing and the combustion conditions necessary for the oxidation reaction to occur. While the laboratory studies established the conditions needed to catalytically incinerate tail gas, employing the same catalyst that General Motors uses in automobile catalytic converters, simple economic analysis showed the process did not offer any cost advantages over conventional incineration unless fuel gas costs rise substantially above 1980 levels. However, it was determined that a combined catalytic/recuperative heat exchange incinerator could generate enough fuel savings to give it an advantage over optimized, conventional incineration.

The Effect of Incinerator Configuration and Waste Gas Fuel Values on the Need for Supplementary Fuel at Sulphur Plants



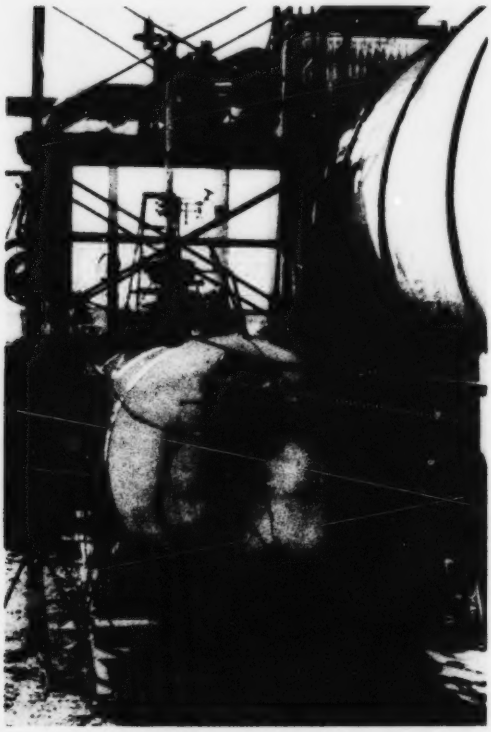
(Source: *Catalytic/Recuperative Incinerator Pilot Plant Investigation*, Paskall, Harold G., R.A. Ritter and P.R. Dale, Bow Valley Research Ltd., June 1985)

Pilot-Scale Studies

Pilot plant-scale studies of recuperative heat exchange and catalytic/recuperative heat exchange incineration were conducted at a sulphur recovery plant.

The recuperative heat exchange incinerator was operated satisfactorily with only half the fuel needed in a conventional incinerator. Although the costs to build a full-scale incinerator were estimated to be 20 per cent higher than a conventional incinerator, cost savings due to reduced fuel demand could result in a payback period of less than one year.

In the case of the pilot catalytic/recuperative heat exchange incinerator, energy savings from 30 to 100 per cent were demonstrated in comparison with conventional incineration, with the added bonus that the concept is flexible enough to take advantage of the inherent heating value of some tail gas streams which contain more combustibles.



The catalytic/recuperative pilot incinerator used in one of Bow Valley's research studies. Beside it is a full-scale conventional incinerator.

Energy Conservation Strategies

In a related study of energy consumption in the natural gas industry as a whole, it was found that 5.6 per cent of all the natural gas recovered for sale is consumed in preparing the product for market. Depending on the variable characteristics of the gas itself, and the types of processing that are required, the principal energy-consuming operations were shown to be compression, process heating, steam generation, waste gas incineration and acid gas removal. Analysis of these operations showed energy consumption in the natural gas industry could be reduced by up to 20 per cent through various energy conservation measures.

Subsequently, an energy audit strategy was developed which was shown to be versatile enough to be easily applied to the diverse operating conditions prevalent in Alberta's natural gas industry.

The strategy is cyclical in nature. It is first applied to obtain an overview of energy distribution and usage and then it is reapplied in descending order of energy consumption. Thus, each cycle is concerned with lesser amounts of consumed energy. In this manner the results of one cycle can be used to indicate whether a succeeding cycle is worthwhile in terms of potential energy savings. A small plant might require two or three cycles whereas larger facilities may need up to eight cycles.

Subsequent Developments and Further Reading

Because of the economic downturn in the early '80s, followed by lower commodity prices a few years later, members of the natural gas industry have decided to defer implementation of the process modifications developed during this series of research investigations. However, direct and indirect benefits to Bow Valley/Western Research have included sales of more than 170 small, waste gas incinerators which were developed and manufactured in-house, as well as sales of process instrumentation, and contracts to provide consulting services. Each of these services has helped enhance the reputation of the contractors in this field.

Persons interested in learning more about these studies should refer to the following technical reports:

Berlie, E.M., R.A. Ritter and J.A. Sames. 1982. *Energy Consumption in the Natural Gas Industry*, Bow Valley Research Ltd.

Colley, D.G., R.A. Ritter and R.E. Hensley. 1981. *Recuperative Heat Exchange Incinerator Pilot Plant*, Bow Valley Research Ltd.

Paskall, Harold, G. 1979. *Capability of the Modified Claus Process*, Western Research and Development.

Paskall, Harold G. 1981. *Catalytic Incineration of Sulphur Plant Waste Gases*, Bow Valley Research Ltd.

Paskall, Harold G., R.A. Ritter and P.R. Dale. 1985. *Catalytic/Recuperative Incinerator Pilot Plant Investigation*, Bow Valley Research Ltd.

Paskall, Harold G., R.A. Ritter, J.A. Sames and P.R. Dale. 1985. *An Energy Audit Strategy for Gas Plants*, Bow Valley Research Ltd.

Ritter, R.A. 1978. *Claus Plant Waste Gas Incinerators*, Western Research and Development.

Contacts

For further information regarding the Pronk Sulphur Asphalt Paving Process contact:

Dr. D.R. Muir
President
Sulphur Development Institute of Canada
Suite 1702
505 - 3rd Street, S.W.
Calgary, Alberta
T2P 3E6

Telephone: (403) 265-4220

Details regarding the evaluation of Claus catalysts are available from:

Dr. I.G. Dalla Lana
Department of Chemical Engineering
University of Alberta
Edmonton, Alberta
T6G 2G6

Telephone: (403) 432-3391

Specifics about thermal decomposition of hydrogen sulphide to produce hydrogen and sulphur may be obtained from:

Dr. T. Chivers
Department of Chemistry
University of Calgary
2500 University Drive, N.W.
Calgary, Alberta
T2N 1N4

Telephone: (403) 220-5741

Requests for details regarding the various sulphur plant studies should be directed to:

Dr. R.A. Ritter
Director of Research
Bow Valley Research Ltd.
1313 - 44 Avenue, N.E.
Calgary, Alberta
T2E 6L5

Telephone: (403) 291-1313

Additional copies of this publication are available from:

Alberta Energy Information Centre
Main Floor, Bramalea Bldg.
9920 - 108 Street
Edmonton, Alberta
T5K 2M4

Telephone: (403) 427-3590

For more information about A/CERRF, contact:

Director, Energy Conservation
and Renewable Energy Research
Scientific and Engineering Services and Research Division
Alberta Energy
2nd Floor Pacific Plaza
10909 Jasper Avenue
Edmonton, Alberta
T5J 3M8

Telephone: (403) 427-8042